

# PATENT SPECIFICATION

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## (54) PACKAGE FOR SEA DISPOSAL OR STORAGE ON LAND OF RADIOACTIVE OR INDUSTRIAL WASTE

(71) We, JAPAN ATOMIC ENERGY RESEARCH INSTITUTE and CHICHIBU CEMENT CO., LTD., Japanese body corporates of No. 1-13, Shinbashi 1-chome, Minato-ku, Tokyo, Japan and 4-6, Marunouchi 1-chome, Chiyoda-ku, Tokyo, Japan, respectively, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

### 1. *Field of the Invention*

This invention relates to a package for sea disposal or storage on land of radioactive or industrial waste.

### 2. *Description of the Prior Art:*

In recent years, radioactive waste generated at nuclear power plants and other atomic energy facilities and industrial waste have been increasing and it is, therefore, an urgent problem to establish a safe disposal and storage system for radioactive waste or industrial waste.

It is estimated that the amount of low-radioactivity waste generated in Japan will be 245,000 drums per year by 1985 and that by that time the accumulated total may be 1,350,000 drums. Therefore, a large land area and a huge amount of money are required in order to store all of the radioactive waste. Therefore, small countries the population density of which is high, such as Japan and various countries in Europe, are pressing for the establishment of sea disposal of radioactive waste. The Japanese Government will confirm safety and establish sea disposal techniques on its own responsibility with the cooperation of the agencies concerned both at home and abroad, as well as on the basis of the advance assessment of the possible effects on the environment of sea disposal in light of surveys so far conducted on the sea environment and 10 years of experience in sea disposal by the Nuclear Energy Agency (NEA) of the Organization for Economic Cooperation and Development (OECD).

The judgement and disposal and storage of harmful waste other than radioactive waste are controlled by the "Waste Disposal and Public Cleaning Law", "Determination Method of Harmful Substances in Industrial Waste". The Prime Minister's Office Order Providing Determination Standard Regarding Harmful Industrial Waste" and so forth. Sea disposal of cadmium, lead, organic phosphate, arsenic and chromium hexavalent by cement solidification is stipulated in the statutes. Cyanides and mercury over standard value are also subject to cement solidification. Regarding land disposal thereof, cement solidification is stipulated or recommended in the statutes.

Conventional disposal and storage techniques of radioactive waste and industrial waste are outlined below:

Sea disposal of high-radioactivity waste is prohibited, but with respect to medium- and low-radioactivity waste, such means as cement or asphalt may be used to solidify them in monolithic drums or multi-stage soft steel (SS) drums. Then they are to be dropped where the sea is 3,000 or more metres deep. The drum packages are easy to handle and relatively inexpensive and have conventionally given satisfactory results. But, the drum packages suffer from the defect that the durability under high hydraulic pressure is not satisfactory and, because of corrosion of the drum by sea water, the radioactive materials are apt to leach from the package. When the amount of waste discarded is small, this defect can be neglected, but when a large amount of radioactive waste is discarded over many years, this defect causes sea

pollution. On the other hand, if a stainless steel drum is used in order to improve the anti-corrosive property of the sea disposal package, the stainless steel drum should have sufficient thickness to withstand transport and high hydraulic pressure and it is, therefore, very expensive. And what is worse, the stainless steel is apt to be corroded with corrosive ions such as  $\text{Cl}^-$ ,  $\text{NH}_4^+$ , and so forth, and therefore, the stainless steel drum may be corroded gradually over a long term even if it is used not in the sea but on land. For the reasons stated above, the stainless steel drum is rather impractical.

A solidified waste comprising a mixture of concrete and various kinds of waste including radioactive waste, heavy metals and so forth becomes a porous structure having many voids and irregularly interconnected cells because of air entrained during the mixing step and bleeding during the curing step. Therefore, the sea water permeates easily into the solidified waste and this causes the leaching of radioactive substance, heavy metals and so forth. Especially when surface active agents are included in the waste and when the proportion of water to cement is high, the mixing can not be effected sufficiently and the solidified waste formed becomes a porous structure and consequently, the waste leaches more easily.

Furthermore, it is well known that the cement solidified ion-exchange resin loses strength or swells to disintegrate when it is soaked in water.

When the concentrated liquid waste released from a BWR atomic power plant is solidified with conventional Portland cement, it forms an ettringite in water, because the major component of the liquid waste is sodium sulphate and consequently it is liable to expand and be broken. The concentrated liquid waste released from a PWR atomic power plant is solidified in the form of sodium borate, since the major component thereof is boric acid; but this is not strong enough and lacks stability. For the reasons stated above, neither the cement-solidification in the monolithic drum nor the cement-solidification in the multi-stage drum is an ideal disposal and storage system for radioactive waste and industrial waste.

An asphalt-solidification disposal method of radioactive waste has recently become available because it can be carried out inexpensively. However, the asphalt-solidified radioactive waste has several defects; its fire resistance lowers during storage on land and it emits an offensive odour and swells in water at high pressure. In addition, since the specific gravity of the asphalt-solidified radioactive waste is low, the addition of heavy filler thereto is required for sea disposal of the asphalt-solidified radioactive waste.

For the reasons stated above, both the cement-solidification of radioactive waste and the cement- or asphalt solidification of radioactive waste in drums and so forth are unsuitable for either the land storage or the sea disposal of radioactive waste.

The use of a polymer-impregnated concrete package with a monomer such as methyl-methacrylate and polymerising said monomer for a disposal package of radioactive waste and industrial waste has been proposed. A polymer-impregnated concrete package of this kind has high strength and high durability and can prevent leaching of the radio-active substances; however, the impact resistance thereof is not appreciably better than that obtained when concrete only is used and fire-resistance thereof is lowered. Therefore, safe transport and safety at the time of calamities such as earthquake, fires and so forth are not fully guaranteed for the polymer-impregnated concrete package. And furthermore, when a polymer-impregnated concrete package is used for sea disposal of radioactive waste discarded in the deep sea of about 3,000 metres in depth, it collides with rocks on the bottom of the sea and hair cracks are formed in said package, and these hair cracks become water passes and eventually internal pressure of the polymer-impregnated concrete package becomes equal to external pressure and then radioactive substances may easily leak out of the package. For the reasons stated above, a polymer-impregnated concrete package of this kind is not satisfactory for either storage on land or sea disposal of radioactive or industrial waste. In addition the polymer-impregnated concrete package has the defect that its fire-resistance is lowered.

In recent years, steel fibre-reinforced concrete has been used for a wide variety of purposes. The various properties of concrete such as impact resistance, toughness, shearing strength, fatigue performance and so forth are significantly improved by reinforcing the concrete with steel fibre, but, the steel fibre incorporated with concrete is easily corroded and deteriorated in the presence of sea water or acidic water. Furthermore, there are several problems to be solved in manufacturing the steel fibre-reinforced concrete; that is, the steel fibre can not be easily dispersed uniformly in a concrete matrix and consequently, defective concrete, that is, concrete in which cavities or voids are formed, is produced. Therefore, the steel fibre-reinforced concrete package is not suitable for a disposal package of radioactive waste.

Accordingly, an improved package for disposal or storage of radioactive waste or industrial waste without the defects of the conventional packages mentioned above has been desired in the art.

Therefore, the main object of this invention is to provide an improved package for sea disposal or storage on land of radioactive waste or industrial waste and having excellent

strength, impact-resistance, fire-resistance, corrosion-resistance, impermeability to water and so forth.

Another object of this invention is to provide an improved package for sea disposal or storage on land of radioactive waste or industrial waste prepared by impregnating a pre-formed steel fibre-reinforced concrete package with an impregnant such as polymerizing monomer and then polymerizing the monomer in the concrete. These and other objects as well as advantages of this invention will become apparent from the subsequent description.

The present invention provides a package for sea disposal or storage on land of radioactive waste or industrial waste is manufactured by impregnating a precast fibre-reinforced concrete container with a polymerizable impregnant and then polymerizing the impregnant in the concrete matrix by thermal-polymerization or radiation polymerization.

There are three methods of storage of radioactive waste or industrial waste on land; one is storage on the surface, another is storage in a pit or in a tank buried in the ground and another is burial in shallow ground. However, the inventors of this invention use the term "storage on land" as a general name including all three methods of storage of radioactive waste and industrial waste on land as stated above.

A package for the disposal or storage of radioactive waste or industrial waste is manufactured most efficiently by impregnating a precast concrete container and cap prepared by means of vibration-moulding or centrifugal-moulding with polymerizable monomer, polymerizing said monomer by thermal-polymerization or radiation polymerization and then joining the container with the cap by appropriate means. However, taking into consideration that the package of this invention is characterized by the process for manufacturing thereof and the uses thereof rather than the structure and design thereof, various variations and modifications can be made in the structure and the design of the package of this invention without departing from the scope of this invention. For example, the corners of the package may be rounded off to disperse the stress of high hydraulic pressure and impact pressure acting upon the package. Or a cap having a T-shaped cross-section may be used in order to join it with the container easily. Or in some cases, the radioactive waste or industrial waste packed in the package of this invention may be solidified by pouring cement concrete or polymer concrete into the package. Examples of fibre-reinforcing materials for reinforcing the concrete include steel mesh, carbon fibre, nylon fibre, asbestos fibre and steel fibre. However, steel-fibre is preferably used in this invention from the stand-point of economy and strength. And furthermore, an interlock system may be employed in order to join more firmly the container with the cap.

A composite material produced by impregnating steel fibre-reinforced concrete with a polymer is well-known. And it is also well known that toughness, impact-resistance, fatigue-performance and so forth of concrete can be significantly improved by reinforcing the concrete with steel fibre and that resistance to corrosion from sea water, acid-resistance, corrosion-resistance and denseness of concrete can be improved by impregnating the steel fibre-reinforced concrete with polymer. But, the excellent properties of steel fibre-reinforced polymer-impregnated concrete have not yet been put to practical use. The inventors of this invention gave particular attention to the excellent properties of steel fibre-reinforced polymer-impregnated concrete and used the excellent properties for a package for disposal or storage of radioactive waste or industrial waste.

Representative impregnants available for manufacture of the package of this invention are unsaturated esters such as methylmethacrylate, methylacrylate, or ethylacrylate and radical polymerizable vinyl monomers such as styrene, 2-methylstyrene, or acrylonitrile. However, taking into account the particular uses of the package of this invention, the preferred impregnant is selected from the group consisting of radiation-resistant monomers having a benzene ring or a phenol ring such as styrene or phenol and radiation resistant copolymers such as styrene-butadiene copolymer. These monomers or copolymers may be used independently or in combination with each other or with other polymers. A methylmethacrylate monomer in which a polystyrene is dissolved is the most effective impregnant for use in this invention. The molar fraction of the polystyrene dissolved in methylmethacrylate is preferably from 4% to 40%, more preferably from 5% to 20% from the standpoint of solubility of methylmethacrylate in polystyrene and viscosity of the solution formed.

A crosslinking agent conventionally used such as divinylbenzene, trimethylolpropanetrimethacrylate, or polyethyleneglycoldimethacrylate may be used in combination with the impregnant.

Both thermal-polymerization and radiation-polymerization may be adopted in order to polymerize the impregnant in concrete matrix. When a thermal-polymerization method is adopted, a conventional polymerization initiator is used. Representative polymerization initiators are organic azo compounds such as azobisisobutyronitrile, organo-peroxides such as benzoyl peroxide or t-butylhydroperoxide and so forth.

This invention is further illustrated by the following Examples. However, this invention

should not be limited by these Examples.

*Example 1*

A cylindrical container having 380 mm outside diameter, 220 mm inside diameter, 570 mm height and 130 mm bottom thickness was manufactured by a precast method from concrete having slump of 2 cm and comprising 550 Kg/m<sup>3</sup> of cement, 187 Kg/m<sup>3</sup> of water, 639 Kg/m<sup>3</sup> of coarse aggregate and 950 Kg/m<sup>3</sup> of fine aggregate and in which was incorporated 2 percent of steel fibre on the basis of the volume of concrete and cured by steam at 65°C for 3 hours and was then released from the mould. Thereafter, the container was dried at 150°C for 20 hours and was impregnated with methylmethacrylate monomer in which 5% by weight of polystyrene was dissolved and then irradiated with gamma rays from Co-60 at 6 Mrad in water to polymerize and cure the methylmethacrylate monomer in the concrete matrix.

A cap having 380 mm outside diameter and 130 mm thickness manufactured from the same concrete as described above was treated in the same manner as described above.

The cap was placed on the container and the joint sealed with epoxy resin to produce a capped package. After three days, a pressure test was carried out by standing the package at room temperature under an external hydraulic pressure of 500 Kg/cm<sup>2</sup> for 10 minutes.

The package of this invention was proved to be sound by the pressure test. When the maximum stress of the package was measured in the circumferential direction at the central portion of the package it was found that the central portion of the package had contracted about 0.33 mm.

*Example 2*

The steel fibre-reinforced concrete container and cap manufactured in the same way as described in Example 1 respectively were impregnated with methylmethacrylate monomer in which 1% by weight of azobisisobutyronitrile was dissolved and then the container and cap were permitted to stand in water at 80°C for one hour to polymerize and cure the monomer in the concrete matrix. The thus manufactured steel fibre-reinforced polymer-impregnated concrete was then capped and the joint sealed by epoxy resin to produce a package. After three days, a pressure test was carried out by standing the package at ambient temperature under an external hydraulic pressure of 500 Kg/cm<sup>2</sup> for ten minutes.

The package of this invention was proved to be sound by the pressure test. When the maximum stress of the package was measured in the circumferential direction at the central portion of the package, it was found that the central portion of the package has contracted about 0.34 mm.

*Example 3*

A steel fibre-reinforced polymer-impregnated concrete package was manufactured in the same way as described in Example 1.

A pressure test was carried out on the package by standing the container under the same conditions in the sea at a depth of 5,000 metres (pressure of 500 Kg/cm<sup>2</sup>, water temperature of 2°C, flow rate of water of 1 - 2 cm/sec) for 110 hours.

No breakage and no leakage of water were observed during the pressure test.

*Example 4*

Sham radioactive waste with a specific gravity of 2.0 was solidified and packed in a package manufactured in the same way as described in Example 1. The package was dropped from a height of 60 cm onto a concrete plate 25 cm in thickness resting on a firm foundation to carry out a drop-impact resistance strength test. There was no breakage. The impact imparted to the package when it is dropped from a height of 60 cm corresponds to the impact imparted to the package when it strikes the sea bed, so it is clear that the package of this invention has excellent impact resistance and is suitable for sea disposal.

*Example 5*

A steel fibre-reinforced polymer-impregnated concrete package was manufactured in the same way as described in Example 1.

The ultimate strength of the package was measured by an external pressure testing machine and the measured flexural tensile strength was 216.8 Kg/cm<sup>2</sup>.

*Example 6*

A steel fibre-reinforced polymer-impregnated concrete package manufactured in the same way as described in Example 1 was joined with bolts. After 7 days, a drop-impact resistance strength test was carried out by dropping the package onto a concrete plate 25 cm in thickness resting on a firm foundation. No change was observed in the package dropped from a height of 60 cm. When dropped from a height of 120 cm, the package dropped with a slight gradient and a few hair cracks were observed in the epoxy resin joint between the cap and container, but no change was observed in the body of the package.

*Example 7*

A steel fibre-reinforced polymer impregnated concrete container and cap manufactured in the same way as described in Example 1 were fastened together with epoxy resin and then

reinforced with four bolts to produce a sealed package. A fire-resistance test was carried out for the package. That is to say, the package was set in a pan made of iron containing 50 l of kerosene, and subjected to flames for about 30 minutes. Immediately after the burning of the kerosene, the package was quenched rapidly by wetting with a fire hose. In this test, melting of the epoxy resin joint between the container and the cap and melting of the polymer incorporated in the concrete matrix were observed. However, no cracks or breaks were observed in the body of the package during and after the burning of the kerosene. Furthermore, the package could be lifted and transported by means of the bolts embedded in the cap.

*Reference Example 1*

A container and cap which have the same size as described in Example 1 respectively were manufactured from plain concrete, that is concrete not reinforced by steel fibre. The container and the cap were fastened together with epoxy resin to produce a capped package. The package was then subjected to a pressure test in the same way as disclosed in Example 1. In the course of raising the pressure up to 500 Kg/cm<sup>2</sup>, the central portion of the package imploded at a pressure of 423 Kg/cm<sup>2</sup>.

*Reference Example 2*

A steel fibre-reinforced concrete container and cap manufactured in the same way as described in Example 1 were fastened together with epoxy resin to produce a capped package. The package was then subjected to pressure test in the same way as disclosed in Example 1.

In the course of raising the pressure up to 500 Kg/cm<sup>2</sup>, water leaked into the package at a pressure of approximately 100 Kg/cm<sup>2</sup>. Pinholes were observed in the bottom of the package.

*Reference Example 3*

A package made in the same way as the package used in Reference Example 1 was subjected to a drop-impact resistance strength test in the same way as described in Example 4. Hair cracks passing through the package were observed.

*Reference Example 4*

A package made in the same way as the package used in Reference Example 3 was impregnated with methylmethacrylate monomer in which 5% by weight of polystyrene was dissolved and irradiated with gamma rays from Co-60 at 8Mrad in water to polymerize and cure the monomer in the concrete matrix. Then the package was subjected to the drop-impact resistance strength test in the same manner as described in Example 4. Hair cracks were observed in the package; however, the magnitude of the hair cracks was relatively small compared to those observed in Reference Example 3.

*Reference Example 5*

A steel fibre-reinforced concrete package was manufactured in the same way as described in Example 1 except that the package was not impregnated with polymer. The package was then subjected to a breaking strength test by using an external pressure testing machine. The measured flexural tensile strength was 125.8 Kg/cm<sup>2</sup>.

*Reference Example 6*

A test specimen was made of conventional concrete having slump of 2 cm comprising 500 Kg/cm<sup>3</sup> of cement, 200 Kg/m<sup>3</sup> of water, 830 Kg/m<sup>3</sup> of coarse aggregate and 800 Kg/m<sup>3</sup> of fine aggregate by a precasting method and cured. The test specimen was subjected to a breaking strength test by using an external pressure testing machine. The measured bending tensile strength was 58.4 Kg/cm<sup>2</sup>.

*Reference Example 7*

A test specimen made in the same way as the test specimen used in Reference Example 6 was impregnated with methylmethacrylate monomer in which 5% by weight of polystyrene was dissolved and then irradiated with gamma rays from Co-60 at 6Mrad in water to polymerize and cure the monomer. The test specimen was subjected to a breaking strength test by using an external pressure testing machine. The measured flexural tensile strength was 155.4 Kg/cm<sup>2</sup>.

*Reference Example 8*

A container and a cap were manufactured from concrete having the same components as used in Example 1. The container and cap were fastened together with epoxy resin to form a capped package which was then joined in four places with bolts. The bolt-joined package was then subjected to a drop-impact resistance strength test. When dropped from a height of 60 cm, no change was observed in the package, but when dropped from a height of 120 cm, a few hair cracks were observed in the package.

*Reference Example 9*

A container and a cap were manufactured from the concrete used in Reference Example 6. The container and the cap were impregnated with methylmethacrylate monomer and irradiated with gamma rays from Co-60 at 6 Mrad to polymerize and cure the monomer. The container and cap were fastened together with epoxy resin to produce a capped package

which was then joined in four places with bolts. The thus bolt-joined package was subjected to a drop-impact resistance strength test in the same way as described in Example 6. When the package was dropped from a height of 60 cm, a few hair cracks were observed in the package, and when dropped from a height of 120 cm, a large number of hair cracks was observed in the package.

Comparing Example 6 with Reference Examples 8 and 9, it is clear that the package made of steel fibre-reinforced polymer-impregnated concrete is significantly superior in drop-impact resistance.

*Reference Example 10.*

A test specimen was prepared from the same concrete as used in Reference Example 6 and impregnated with polymer. Then the polymer-impregnated specimen was subjected to a fire-resistance test. A number of hair cracks was observed in the specimen. And when the specimen was beaten with a hammer after the fire-resistance test, the portion of the specimen outside the reinforcing bars crumbled to pieces.

It is proved by Examples and Reference Examples as stated above that the steel fibre-reinforced polymer-impregnated concrete package of this invention is significantly superior for sea disposal or storage on land of radioactive waste or industrial waste.

**WHAT WE CLAIM IS:-**

1. A package for sea disposal or storage on land of radioactive waste having improved strength, impact-resistance, corrosion-resistance, impermeability to water and fire-resistance which is produced by impregnating a precast fibre-reinforced concrete container with a polymerizable impregnant and the polymerizing the impregnant in the concrete matrix, by thermal polymerization or radiation polymerization.

2. A package as claimed in Claim 1, wherein the polymerizable impregnant is selected from the group consisting of polymerizable monomer, mixture of polymerizable monomer with oligomer, polymer solution in monomer, copolymer solution in monomer and mixtures thereof.

3. A package as claimed in Claim 1, wherein the polymerizable impregnant is selected from the group consisting of radiation-resistant monomer, radiation-resistant polymer and mixtures thereof.

4. A package as claimed in Claim 1, wherein the polymerizable impregnant is a methylmethacrylate solution of polystyrene.

5. A package as claimed in Claim 1, wherein the molar fraction of the polystyrene is from 4% to 40%, preferably from 5% to 20%.

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